

PATENT SPECIFICATION

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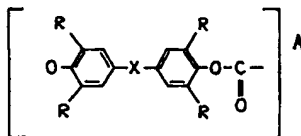


(54) PROCESS FOR THE MANUFACTURE OF SAPONIFICATION-RESISTANT BLOCK COPOLYCARBONATES

(71) We, BAYER AKTIENGESSELLSCHAFT formerly known as Farbenfabriken Bayer Aktiengesellschaft, a body corporate organised under the laws of Germany, of 509 Leverkusen-Bayerwerk, Germany, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

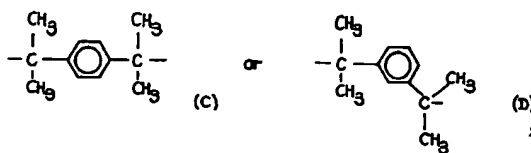
This invention relates to the production of saponification-resistant aromatic block copolycarbonates.

This invention relates to the production of saponification-resistant aromatic block copolycarbonate containing at least 50 mol percent of identical or non-identical structural units of the general formula:—

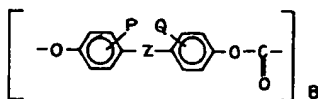


in which R is —CH₃, C₂H₅, or —CH(CH₃)₂, and

X is a single bond, an alkylene or alkylidene group with up to 5 carbon atoms, a cycloalkylidene or cycloalkylene radical with 5 to 15 carbon atoms, —O—, —CO—,



and at most 50 mol percent of identical or non-identical structural units of the general formula:—

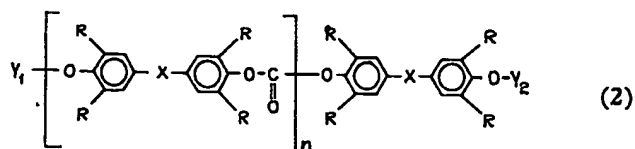


in which Z can have any of the meanings given above for X and in addition can be —SO₂—; and

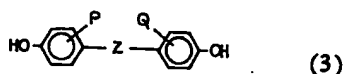
P and Q are each from 0 to 4 substituent groups, with the proviso that the o,o',o'-tetra alkyl substituted units of the formula A are excluded.

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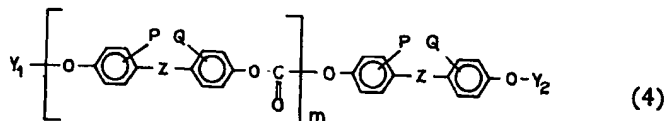
The process for the production of the copolycarbonates defined above comprises the reaction of at least one low molecular weight polycarbonate of the general formula:—



5 with at least one aromatic dihydroxy compound of the general formula:—

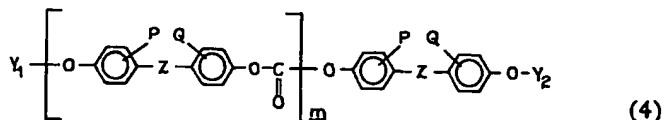


or the mono- or bis-chlorocarbonic acid ester thereof, or with at least one low molecular weight polycarbonate of the general formula:—

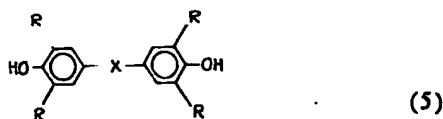


10 optionally in the presence of phosgene, in a two-phase mixture of an inert organic solvent and an aqueous-alkaline phase in the presence of 0.012 to 0.3 mol of at least one tertiary amine per litre of two-phase mixture, the ratio of the reactants of general formula 2, 3 and 4 being so chosen that at most equimolar amounts of the radicals of general formula B relative to the molar amounts of the radicals of general formula A enter into the polymer, and at least 1.05 chlorine equivalents bonded via C=O are present per —OH equivalent; in which general formulae X, Z, P, Q and R are as defined above; Y₁ and Y₂ which may be the same or different, are each —H or —CO.Cl; n is 4 to 30; and m is 1 to 30, preferably 4 to 30.

The invention further provides a second process for the production of the copolycarbonates defined above, which comprises the reaction of at least one low molecular weight polycarbonate of the general formula:—



25 with at least one bisphenol of the general formula:—



or the mono- or bis-chlorocarbonic acid ester thereof, optionally in the presence of phosgene, in a two-phase mixture of an inert organic solvent and an aqueous-alkaline phase in the presence of 0.012 to 0.3 mol of at least one tertiary amine per litre of two-phase mixture, the ratio of the reactants of general formulae (4) and (5) being so chosen that at most equimolar amounts of the radicals of general formula B relative to the molar amounts of radicals of general formula A enter into the polymer, and at least 1.05 chlorine equivalents bonded via C=O are present per —OH equivalent, in which general formulae (4) and (5) X, Y₁, Y₂, Z, P, Q, R, and n are as defined above, and m is 4 to 30.

The reactions according to the invention may if desired be carried out in the presence of at least one chain stopper.

The compounds of the general formulae 3 and 4 (or the radical B) are optionally nuclear substituted by one or more substituents P and Q, with the proviso that the compounds of general formulae 2 and 5 (or the radical A) are excluded; these substituents can in particular be halogen atoms, such as chlorine and bromine atoms.

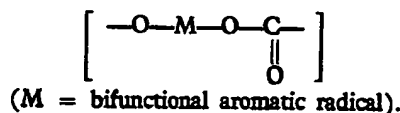
In the processes of the invention, reaction times of 0.05 to 5 hours are generally necessary.

The copolycarbonates prepared by the process of the invention are generally of high molecular weight, that is, they preferably have a molecular weight of above 20,000.

The copolycondensation according to the invention in the presence of such high amine concentrations to give high molecular block copolycarbonates, with quantitative conversion of the starting compounds, was not to be expected. Thus, for example, in the reaction of 2,2-bis-(4-hydroxyphenyl)-propane with phosgene small amounts of amine, for example 0.0005—0.0015 mol of triethylamine/l of two-phase mixture already suffice in order to manufacture high molecular polycarbonates in a short time (5—15 minutes). On the other hand, a higher amine concentration, 0.004—0.010 mol of triethylamine/l of two-phase mixture, admittedly also still gives high molecular polycarbonates, but here the conversion of bisphenol A is greatly reduced so that with increasing amount of amine increasing proportions of bisphenol remain in the aqueous alkaline phase.

Equally, as emerges from German Auslegeschrift (German Published Specification) 1,190,185 (Page 1), amine concentrations of more than 1.0 mol %, relative to the bisphenol present, are disadvantageous to the formation of polycarbonate if phenol or substituted phenols are used as chain stoppers.

The processes according to the invention have numerous advantages over the process known from German Offenlegungsschrift (German Published Specification 1,570,703), which consists of the manufacture of block copolycarbonates with blocks averaging 15 to 25 units of a comparable type of the formula A, linked via different structural units of type B



in a homogeneous inert organic phase containing pyridine.

The working up of the solution is facilitated, since the organic solutions can, without pyridine, be separated more easily from the aqueous phase after washing. The recovery of pyridine necessary after the process of German Offenlegungsschrift (German Published Specification) 1,570,703 is dispensed with.

The processes according to the invention furthermore possess greater versatility. This is because, whilst in the process of German Offenlegungsschrift (German Published Specification) 1,570,703 it is always only possible to link low molecular polycarbonates based on o,o',o'-tetra-alkyl-substituted bisphenols by means of other bisphenols and phosgene to give high molecular block copolycarbonates, it is for example possible, according to the process of the invention, also to link blocks of o,o',o'-tetra-alkyl-substituted bisphenols with blocks of other bisphenols. Furthermore it is possible for example, to react low molecular polycarbonates with OH end groups from bisphenols unsubstituted in the o,o',o'-position with bis-chlorocarbonic acid esters of o,o',o'-tetra-substituted bisphenols to give high molecular block copolycarbonates, whilst this is not possible according to the process of German Offenlegungsschrift (German Published Specification) 1,570,703.

Furthermore, as a result of the possibility of obtaining extremely high molecular

weight blockpolycarbonates, it is possible accurately to choose the desired molecular weights by the addition of defined amounts of chain stoppers. Furthermore, polycarbonates are obtained which no longer contain saponifiable chlorine from chlorocarbonic acid ester end groups.

The polycarbonates obtained in accordance with the processes of the present invention show particularly good mechanical properties, for example elongations at break of $\epsilon_B = 70\%$ (see Examples 6 + 6a); they have non-uniformities

$$U(U = (\bar{M}_w/\bar{M}_n) - 1)$$

of 0.7 to 0.9 and glass temperatures of $>150^\circ\text{C}$.

The bisphenol of formula (5) may, for example, be one of the following bisphenols: bis - (3,5 - dimethyl - 4 - hydroxyphenyl) - methane, bis - (3,5 - diisopropyl - 4 - hydroxyphenyl) - methane, 2,2 - bis - (3 - methyl - 5 - isopropyl - 4 - hydroxyphenyl) - propane, 2,2 - bis - (3,5 - dimethyl - 4 - hydroxyphenyl) - propane, 2,2 - bis - (3,5 - diethyl - 4 - hydroxyphenyl) - propane, 3,3 - bis - (3,5 - dimethyl - 4 - hydroxyphenyl) - pentane, 1,1 - bis - (3,5 - dimethyl - 4 - hydroxyphenyl) - cyclohexane, 1,4 - bis - (3,5 - dimethyl - 4 - hydroxyphenyl) - cyclohexane, bis - (3,5 - dimethyl - 4 - hydroxyphenyl) - ether, bis - (2,5 - dimethyl - 4 - hydroxyphenyl), bis - (3,5 - dimethyl - 4 - hydroxyphenyl) - carbonyl, α,α' - (3,5 - dimethyl - 4 - hydroxyphenyl) - *p* - diisopropylbenzene and α,α' - (3,5 - dimethyl - 4 - hydroxyphenyl) - *m* - diisopropylbenzene.

The synthesis of these bisphenols, where it is not already known, is described in Patent Application 59634/71, (Serial No. 1,367,788).

Examples of other aromatic dihydroxy compounds which can be copolycondensed with the tetra-alkyl-substituted bisphenols of the formula (5) are hydroquinone, resorcinol, dihydroxydiphenyls, bis-(hydroxyphenyl)-alkanes, bis-(hydroxyphenyl)-cycloalkanes, bis-(hydroxyphenyl)-sulphides, bis-(hydroxyphenyl)-ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulphoxides, bis-(hydroxyphenyl)-sulphones, α,α' -bis-(hydroxyphenyl)-diisopropylbenzenes and their nuclear-halogenated and nuclear-alkylated compounds exceptionally those corresponding to formula (5). These and further suitable aromatic dihydroxy compounds are described in U.S. Patent Specifications 3,028,365; 2,999,835; 3,148,172; 3,271,368; 2,991,273; 3,271,367; 3,280,078; 3,014,891 and 2,999,846 and in German Offenlegungsschrift (German Published Specification) 1,570,703. Some examples of preferred bisphenols are 4,4'-dihydroxyphenyl, 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)propane and α,α' -bis-(4-hydroxyphenyl)-*p*-diisopropylbenzene.

According to the processes of the invention, the block copolycarbonates described are obtained in a phase boundary (interfacial) condensation in which the reaction of the starting compounds (oligomeric carbonates, low molecular weight polycarbonates, mono- and bis-chlorocarbonic acid esters based on the aromatic dihydroxy compounds described and COCl_2) takes place under the initially mentioned conditions in the presence of aqueous alkali in a solvent suitable for the block copolycarbonates and the further condensation to give high molecular polycarbonate takes place by addition of at least 0.012 mol of tert. amine/1 of two-phase mixture. For example, the various low molecular weight polycarbonates to be reacted can be conjointly dissolved in a solvent suitable for the block copolycarbonate produced and aqueous alkali, preferably sodium hydroxide solution or potassium hydroxide solution, can be added.

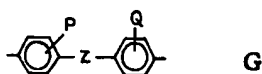
Suitable solvents are, in general, chlorinated paraffins, such as methylene chloride, chloroform and 1,2-dichloroethane, but chlorinated aromatic compounds, such as chlorobenzene, dichlorobenzene and chlorotoluene, are also suitable.

Suitable aqueous alkaline phases are solutions of LiOH , NaOH , KOH , $\text{Ca}(\text{OH})_2$ and/or $\text{Ba}(\text{OH})_2$. The composition of the two-phase mixture generally consists of 0.3 to 3.0 parts of aqueous alkali metal hydroxide or alkaline earth metal hydroxide solution per part of organic solvent phase.

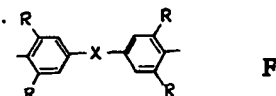
If the low molecular weight polycarbonates do not contain an amount of chlorocarbonic acid ester end groups which suffices for the formation of high molecular weight polycarbonates (it is possible to determine these end groups in accordance with known methods), bis-chlorocarbonic acid esters of aromatic dihydroxy compounds can be added or COCl_2 can be passed in with vigorous stirring.

The reaction, according to the invention, of the compounds of the formulae 2, 3, 4 and 5 can be carried out in any desired molar quantity ratio but must be calculated in such a way that per OH equivalent at least 1.05, including the phosgene, of chlorine

equivalents bonded via $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$ are present during the reaction, and that at most equimolar amounts of radicals of the formula G



relative to molar amounts of radicals of the formula F



in which P, Q, R, X and Z have the meaning described above, participate in the reaction.

The reaction temperature can be 10 to 90°C.

As chain stoppers it is possible to use, for example, phenol, 2,6-dimethylphenol, or p-tert-butylphenol, which are added before the polycondensation catalysed by the addition of tertiary amine. Suitable tertiary amines are, for example, trimethylamine, triethylamine, dimethylbenzylamine or triethylenediamine. The amounts of amine are 0.012 mol/l — 0.3 mol/l of two-phase mixture, preferably 0.015, and in general a reaction time of 5 — 1.5 hours is sufficient. The block copolycarbonates manufactured in this way can be isolated in accordance with known processes, for example if the aqueous phase is separated off, the organic phase is repeatedly washed with water until free of electrolyte and thereafter the block copolycarbonate is precipitated or the solvent is evaporated off. The block copolycarbonates thus obtained do not contain any saponifiable chlorine constituents.

Suitable precondensates (oligomeric carbonates or low molecular weight polycarbonates) for the manufacture of the block copolycarbonates according to the invention can be obtained by the various known ways. It is possible to use precondensates with OH end groups and/or chlorocarbonic acid ester end groups. Some such processes are the melt trans-esterification of bisphenols with diaryl carbonate in the presence of alkaline catalysts (— this process leads to polycarbonate blocks which possess OH end groups —), the reaction of bisphenols in a homogeneous phase, in the presence of an acid acceptor, with phosgene and the phosgenation of bisphenols in a two-phase system, for example CH_2Cl_2 /aqueous NaOH, with optional subsequent condensation of the phosgenation products with catalysts, such as, for example, triethylamine, up to a certain degree of condensation. Examples 1 — 4 describe the manufacture of some pre-condensates. The chain length of the high molecular weight block copolycarbonates can be restricted by addition of chain stoppers during the manufacture of the pre-condensates. However, chain stoppers can also be added later (see Example 6a).

In the examples, \bar{M}_{os} is the osmometrically determined molecular weight and the relative viscosity (η_{rel}) is measured as an 0.5% strength solution in CH_2Cl_2 at 25°C.

Example 1.

Carbonate polymer from 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane and its bis-chlorocarbonic acid ester, manufacture in the homogeneous phase.

114 g (0.4 mol) of 2,2-bis-3,5-dimethyl-4-hydroxyphenyl-propane, 135 g (0.35 mol) of bis-chlorocarbonic acid ester of 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane and 79 g (1 mol) of anhydrous pyridine are added to 1.5-l of anhydrous CH_2Cl_2 . The mixture is stirred for 3 hours. Thereafter the batch is shaken with dilute hydrochloric acid until it is acid and is subsequently washed with water until free of electrolyte. The CH_2Cl_2 is distilled off and the residual resin is dried for 15 hours in a vacuum drying cabinet at 80°C. 222 g of brittle resin having a molecular weight $\bar{M}_{os} = 4,500$ are obtained, containing less than 0.1% of saponifiable chlorine.

Example 2.

Carbonate polymer from 2,2-bis-(4-hydroxyphenyl)-propane and its bis-chloro-carbonic acid ester, manufacture in the homogeneous phase.

114 g (0.5 mol) of 2,2-bis-(4-hydroxyphenyl)-propane, 141 g (0.4 mol) of bis-chlorocarbonic acid ester of 2,2-bis-(4-hydroxyphenyl)-propane and 95 g (1.2 mols) of anhydrous pyridine are added to 1.5 l of anhydrous CH_2Cl_2 . The mixture is stirred for 3 hours. Thereafter the batch is worked up as described in Example 1. 215 g of brittle resin of molecular weight $\bar{M}_{os} = 2,300$ are obtained, containing less than 0.1% of saponifiable chlorine.

Example 3.

Carbonate polymer from 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, manufacture in a two-phase system.

18.4 g (0.46 mol) of NaOH are dissolved in 600 ml of H_2O . 600 ml of CH_2Cl_2 and 56.8 g (0.2 mol) of 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane are added thereto and 0.6 mol (41.8 ml at 0°C) of gaseous phosgene are passed in whilst stirring. During the introduction of the phosgene, the pH value is kept at 13 by dropwise addition of 50% strength NaOH. The aqueous solution is free of bisphenol. After the addition of 2.4 ml (0.02 mol) of triethylamine the mixture is vigorously stirred for 1 hour; at the same time the pH value is kept at pH 13 by dropwise addition of 50% strength NaOH. The entire reaction is carried out under N_2 and at $20 - 25^\circ\text{C}$. The immediately subsequent working up of a fifth of the batch is carried out as indicated in Example 1. The organic phase is free of bisphenol. A brittle oligocarbonate is obtained, $\bar{M}_n = 3,300$. The further 4/5 of the batch are used as described in Example 8.

Example 4.

Carbonate polymer from 2,2-bis-(4-hydroxyphenyl)-propane, manufacture in a two-phase system.

7.2 g (0.18 mol) of NaOH are dissolved in 200 ml of H_2O . 200 ml of CH_2Cl_2 and 18.2 g (0.08 mol) of 2,2-bis-(4-hydroxyphenyl)-propane are added thereto and 0.22 mol (15 ml at 0°C) of phosgene are introduced as a gas, whilst stirring. During the introduction of the phosgene, the pH value is kept at 13 by dropwise addition of 50% NaOH. The aqueous solution is free of bisphenol. After addition of 2 ml of 1% strength aqueous triethylamine solution the mixture is vigorously stirred for 17 minutes; during this time, the pH value is kept at pH 13 by dropwise addition of 50% strength NaOH. The entire reaction is carried out under N_2 and at $20 - 25^\circ\text{C}$. The immediately subsequent working up of a half of the batch is carried out as indicated in Example 1.

The organic phase is free of bisphenol. A brittle oligocarbonate is obtained, $\bar{M}_n = 2,000$. The second half of the batch is used as described in Example 8.

Example 5.

Block copolycarbonate of carbonate polymer obtained in Example 1 and bis-chloro-carbonic acid ester of 2,2-bis-(4-hydroxyphenyl)-propane.

600 ml of CH_2Cl_2 and 600 ml of H_2O are added to 40.3 g of the carbonate polymer obtained in Example 1 and 24.7 g (0.07 mol) of bis-chlorocarbonic acid ester of 2,2-bis-(4-hydroxyphenyl)-propane. 50% strength aqueous NaOH is added dropwise, whilst stirring, until pH 13 is reached. After addition of 2.8 ml (0.02 mol) of triethylamine, the mixture is vigorously stirred for 3 hours. At the same time the pH value is kept at 13 by dropwise addition of 50% strength NaOH and the temperature is kept at $20 - 25^\circ\text{C}$ through cooling. The working up of the organic phase takes place as indicated for the batch in Example 1. The aqueous phase is free of bisphenol. A tough block copolycarbonate having 65 mol % of formula (A) and of relative viscosity $\eta_{rel} = 2.31$ is obtained. $\bar{M}_w = 178,000$.

Example 6.

Block copolycarbonate of carbonate polymer obtained in Example 2 and bis-chloro-carbonic acid ester of 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane.

600 ml of CH_2Cl_2 and 600 ml of H_2O are added to 5.1 g of the carbonate polymer obtained in Example 2 and 73.6 g (0.18 mol) of bis-chlorocarbonic acid ester of 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane. 50% strength aqueous NaOH is added dropwise, whilst stirring, until pH = 13 is reached. After addition of 2.8 ml (0.02 mol) of triethylamine the mixture is vigorously stirred for 3 hours. At the same time the pH value is kept at 13 by dropwise addition of 50% strength NaOH and

the temperature is kept at 20–25°C by cooling. The working up of the organic phase takes place as indicated for the batch in Example 1. The aqueous phase is free of bisphenol. A tough block copolycarbonate having 90 mol % of formula (A) and of relative viscosity $\eta_{rel} = 2.10$ is obtained. $\bar{M}_w = 163,000$, $\bar{M}_n = 88,000$. Heterogeneity $U = 0.85$, elongation at break $\epsilon_R = 75\%$.

Example 6a.

Repetition of Example 6 with 2,6-dimethylphenol as the chain stopper.

The procedure in Example 6 is repeated, but before the addition of CH_2Cl_2 0.65 g (0.054 mol) of 2,6-dimethylphenol are additionally introduced. The aqueous phase is again free of bisphenol. A tough block copolycarbonate of relative viscosity $\eta_{rel} = 1.30$ is obtained. $\bar{M}_w = 38,100$, $\bar{M}_n = 21,600$, heterogeneity $U = 0.76$, elongation at break $\epsilon_R = 71\%$.

Example 7.

Block copolycarbonates from the carbonate polymers obtained in Example 1 and 2.

600 ml of CH_2Cl_2 and 600 ml of H_2O are added to 43.4 g of the carbonate polymer obtained in Example 1 and 15.2 g of the carbonate polymer obtained in Example 2. 50% strength NaOH is added dropwise, whilst stirring, until pH 13 is reached. 20.9 ml (at 0°C) of phosgene (0.3 mol) are then introduced into the mixture, whilst stirring, the pH being kept at 13 by dropwise addition of 50% strength NaOH and the temperature being kept at 20–25°C. After the introduction of the COCl_2 , 2.8 ml (0.02 mol) of triethylamine are added and the mixture is stirred vigorously for a further 3 hours, whilst keeping the pH at 13 as above. The working up of the organic phase is carried out as indicated for the batch in Example 1. The aqueous phase is free of bisphenol. A tough block copolycarbonate having 70 mol % of formula (A) and of relative viscosity $\eta_{rel} = 1.89$ is obtained. $\bar{M}_w = 137,000$.

Example 8.

Block copolycarbonate from the carbonate polymers of Examples 3 and 4.

The synthesis of the oligocarbonates of Examples 3 and 4 are carried out in such a way that the time of subsequent stirring terminates at the same point. Immediately after the end of the subsequent stirring 4/5 of the batch from Example 3 and half of the batch from Example 4 are brought together and after addition of 0.6 ml of triethyl amine the mixture is vigorously stirred for a further 3 hours. Whilst doing so, the temperature is kept at 20–25°C and the pH value at 13 by dropwise addition of 50% strength NaOH. Working up takes place as indicated in Example 1. The organic phase is free of bisphenol. The resulting block copolycarbonate has 80 mol % of formula (A) and a relative viscosity $\eta_{rel} = 2.40$. $\bar{M}_w = 200,000$.

Table 1: Examples of the resistance of the block copolycarbonates according to the invention to 10% strength aqueous sodium hydroxide at 100°C.

Decreases in weight of pieces of film 4 × 5 cm, approx. 70–100 μm thick, weight 150–200 mg. Before weighing, the pieces of film are washed with water and dried.

Treatment time [hours]	Weight decrease in mg for polycarbonates					
	from bisphenol A	from Example 5	from Example 6	from Example 6a	from Example 7	from Example 8
500	completely dissolved	0 mg	0 mg	0 mg	0 mg	0 mg

Table 2: Examples of the resistance of the block copolycarbonates according to the invention to 10% strength aqueous hydrochloric acid at 100°C.

Pieces of film 70–100 μm thick.

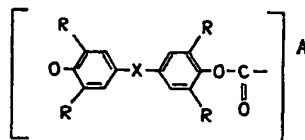
u = unchanged, clear and tough.

Treatment time [hours]	Properties of the polycarbonate films					
	from bisphenol A	from Example 5	from Example 6	from Example 6a	from Example 7	from Example 8
500	disintegrated	u	u	u	u	u

Our co-pending application No. 29027/72 (Serial No. 1,367,789) relates to statistical copolycarbonates comprising at least 50% of structural units of the formula (A).

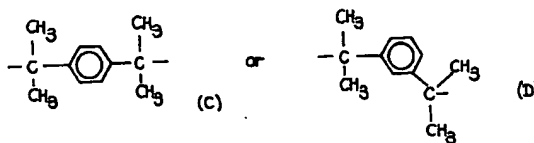
WHAT WE CLAIM IS:—

1. A process for the production of an aromatic block copolycarbonate containing at least 50 mol percent of identical or non-identical structural units of the general formula:—

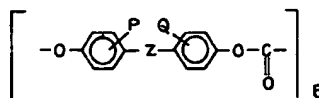


10 in which R is —CH_3 , $\text{—C}_2\text{H}_5$, or $\text{—CH}(\text{CH}_3)_2$ and

X is a single bond, an alkylene or alkylidene group with up to 5 carbon atoms, a cycloalkylidene or cycloalkylene radical with 5 to 15 carbon atoms, —O— , —CO— ,

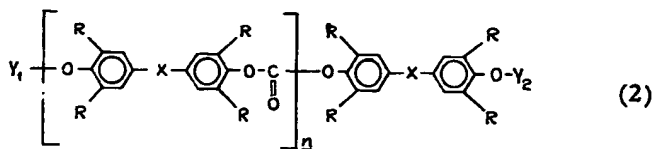


15 and at most 50 mol percent of identical or non-identical structural units of the general formula:—

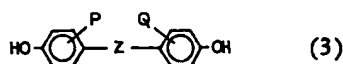


in which Z can have any of the meanings given above for X and in addition can be $\text{—SO}_2\text{—}$; and

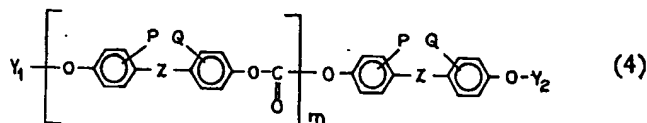
20 P and Q are each from 0 to 4 substituent groups, with the proviso that the structural units A and B are not the same, which comprises the reaction of at least one low molecular weight polycarbonate of the general formula:—



with at least one aromatic dihydroxy compound of the general formula:—



or the mono- or bis-chlorocarbonic acid ester thereof, or with at least one low molecular weight polycarbonate of the general formula:—



optionally in the presence of phosgene, in a two-phase mixture of an inert organic solvent and an aqueous alkaline phase in the presence of 0.012 to 0.3 mol of at least one tertiary amine per litre of reaction mixture, the ratio of the reactants of general formula (2), (3) and (4) being so chosen that at most equimolar amounts of the radicals of general formula B relative to the molar amounts of radicals of general formula A enter into the polymer, and at least 1.05 chlorine equivalents bonded via C=O are present per —OH equivalent;

in which general formulae 2, 3 and 4:—

X, Z, P, Q and R are as defined above

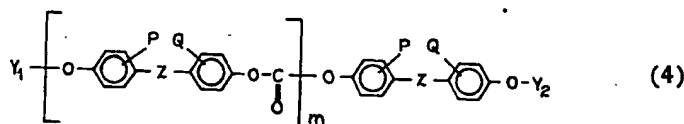
Y₁ and Y₂, which may be the same or different, are each —H or —CO.Cl;

n is 4 to 30; and

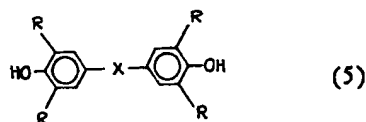
m is 1 to 30.

2. A process according to claim 1 in which m is 4 — 30.

3. A process for the production of the copolycarbonate defined in claim 1 which comprises the reaction of at least one low molecular weight polycarbonate of the general formula:—



with at least one bisphenol of the general formula:—



or the mono- or bis-chlorocarbonic acid ester thereof, optionally in the presence of phosgene, in a two-phase mixture of an inert organic solvent and an aqueous-alkaline phase in the presence of 0.012 to 0.3 mol of at least one tertiary amine per litre of reaction mixture, the ratio of the reactants of general formula (4) and (5) being so chosen that at most equimolar amounts of the radicals of general formula B relative to the molar amounts of radicals of general formula A enter into the polymer, and at least 1.05 chlorine equivalents bonded via C=O are present per —OH equivalent; in which general formulae (4) and (5) X, Y₁, Y₂, Z, P, Q, R, and n are as defined in claim 1 and in which m is 4—30.

4. The process of claim 1, 2 or 3 in which P and Q of the formulae 3 and/or 4 represent at least one halogen atom.

5. The process of claim 3 in which the bisphenol of general formula (5) is one of those hereinbefore mentioned.

6. The process of any preceding claim whenever carried out in the process of a chain stopper.

7. The process of any of claims 1 to 6 in which the solvent is a chlorinated paraffin.

8. The process of any of claims 1 to 7 in which the aqueous-alkaline phase contains sodium or potassium hydroxide.
9. The process of any of claims 1 to 8 in which the two-phase mixture comprises 0.3 to 3.0 parts of aqueous alkaline solution per part of organic solvent.
- 5 10. The process of any of claims 1 to 9 in which the reaction is carried out at 10 to 90°C. 5
11. The process of any of claims 1 to 10 in which 0.015 moles of amine are present per litre of two-phase mixture.
- 10 12. The process of claim 1 or 3 substantially as hereinbefore described, or as illustrated in any of the Examples. 10
13. Polycarbonates whenever produced by the process of any of claims 1 to 12.
14. Polycarbonates whenever produced by the process of claim 2.

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